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Electronic lability in a dinuclear cobalt bis-dioxolene complex

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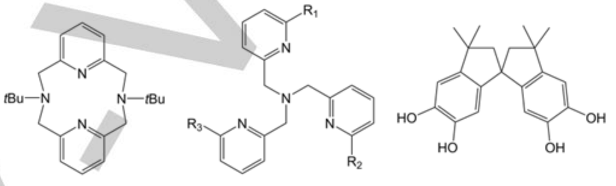
Abstract: Remarkable electronic lability is evident from a preliminary study of a dinuclear cobalt complex with a bis-dioxolene bridging ligand and tetraazamacrocylic ancillary ligands. Structural, magnetic, spectroscopic and electrochemical data indicate coinciding metal and ligand-based mixed-valence involving cobalt(II)/cobalt(III) and catecholate/semiquinonate couples. A thermally-stimulated spin crossover or valence tautomeric transition is also observed above 200 K.

Introduction

Electronically labile molecules can be stimulated to switch reversibly between two electronic forms. They have potential applications in high density data storage, molecular electronics, molecular spintronics or for display devices.[1] Candidate metal complexes undergo spin transitions between low spin (LS) and high spin (HS) forms of the metal and/or intramolecular electron transfer, either between two different metal centers or between a metal center and a redox-active ligand. Cobalt complexes are of considerable interest in this regard, exhibiting both spin crossover (SCO),[2] and valence tautomeric (VT) transitions,[3] which involve intramolecular electron transfer coupled with cobalt-based spin switching. Cobalt-dioxolene complexes provide the most examples of VT transitions,[3] whereby LS-Co^{III}-cat (cat = catecholate) and HS-Co^{II}-sq (sq = semiquinonate) moieties can be interconverted by heating and cooling or irradiation with visible light.[4] Thermally-induced LS-Co^{III}-cat to HS-Co^{II}-sq VT and LS-Co^{II} to HS-Co^{II} SCO transitions are both entropically driven, with the entropy gain arising from the higher spin state degeneracy of the HS-Co^{II}-containing complex and the higher density of vibrational states of this species, due to lengthening of the Co-O/N bonds. While thermally-induced VT transitions have been reported for several complexes of formula $[Co(N_4L)(diox)]^+$, where N_4L is a tetradentate N-donor ligands and diox is a dioxolene ligand (very commonly 3,5-di-*tert*-butyldioxolene),[3,5] the complex $[Co(L\text{-}N_4tBu_2)(3,5\text{-dbsq})]^+$ (**1**), where $L\text{-}N_4tBu_2$ = *N*,*N*'-di-*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane and 3,5-dbsq = 3,5-di-*tert*-butylsemiquinonate, has been reported by Krüger and co-workers to exhibit a SCO transition between LS-Co^{II}-sq and HS-Co^{II}-sq forms.[6] The unusual SCO observed for **1** is attributed to steric requirements of the di-*tert*-butyl substituted tetraazamacrocylic ligand, which favors the Jahn-Teller distorted low spin cobalt(II) state over the low spin cobalt(III) state. Steric requirements of ancillary ligands are also important for VT transitions, with progressive methylation at the 6-position of tris(2-pyridylmethyl)amine (Me_ntpa, n = 0-3) ligands controlling the VT transition temperature of $[Co(Me_ntpa)(diox)]^+$.[5]



L-N_4tBu　　tpa ($R_1 = R_2 = R_3$ = H)
Me_2tpa ($R_1 = R_2$ = Me, R_3 = H)
Me_3tpa ($R_1 = R_2 = R_3$ = Me)　　spiroH_4

In previous work, we have extended to dinuclear cobalt complexes the approach of fine tuning the ancillary ligands to control the charge distribution and VT behavior for complexes incorporating tetradeprotonated 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (spiroH_4) as a bridging ligand. The deprotonated spiro ligand is known to coordinate to metals in the bis-catecholate $(spiro^{cat\text{-}cat})^{4-}$, mixed-valent catecholate-semiquinonate $(spiro^{cat\text{-}sq})^{3-}$ and bis-semiquinonate $(spiro^{sq\text{-}sq})^{2-}$ redox states. We were able to structurally characterize the temperature-invariant complexes $[\{LS\text{-}Co^{III}(tpa)\}_2spiro^{cat\text{-}cat}]^{2+}$ (**2**) and $[\{HS\text{-}Co^{II}(Me_3tpa)\}_2spiro^{sq\text{-}sq}]^{2+}$ (**3**), while the use of Me_2tpa instead gives rise to a two-step VT transition for $[\{Co(Me_2tpa)\}_2spiro]^{2+}$ (**4**).[7,8] Complex **4** can be interconverted between three states in both solution and the solid state involving sequential VT transitions in each half of the dinuclear complex upon heating from $[\{LS\text{-}Co^{III}(Me_2tpa)\}_2spiro^{cat\text{-}cat}]^{2+}$ to $[\{LS\text{-}Co^{III}(Me_2tpa)spiro^{cat\text{-}sq}\{HS\text{-}Co^{II}(Me_2tpa)\}]^{2+}$ and then to $[\{HS\text{-}Co^{II}(Me_2tpa)\}_2spiro^{sq\text{-}sq}]^{2+}$. The key to the two-step VT transition is the small but non-zero electronic communication between the two halves of the spiroconjugated bis-dioxolene bridging ligand.

In the present work we sought to combine the L-$N_4t$$Bu_2$ macrocyclic ancillary ligand with the spiro bis-dioxolene bridging ligand to explore the possibility of electronic lability in the resulting dinuclear cobalt complex. Herein we communicate the initial product of this investigation: the target complex $[\{Co(L\text{-}N_4tBu_2)\}_2(spiro)]^{2+}$ (**5**), which crystallizes as the solvated tetrachlorocobaltate(2-) salt $[\{Co(L\text{-}N_4tBu_2)\}_2(spiro)][CoCl_4]\cdot 5MeCN\cdot H_2O$ (**5a**). Upon air-drying this becomes $[\{Co(L\text{-}N_4tBu_2)\}_2(spiro)][CoCl_4]\cdot 3H_2O$ (**5b**).

Results and Discussion

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The ancillary ligand L-N_4tBu_2 was synthesized according to literature procedures.[9] The synthesis of complex **5** (Figure 1) involved the combination under an inert atmosphere of stoichiometric quantities of cobalt(II) chloride with L-N_4tBu_2 and then with deprotonated (spiro$^{cat-cat}$)$^{4-}$, before exposure to air to allow partial oxidation. The crystals of **5a** must be isolated immediately upon formation, as they tend to redissolve. The complex was isolated in modest yield as the blue crystalline tetrachlorocobaltate(2-) salt **5b**.

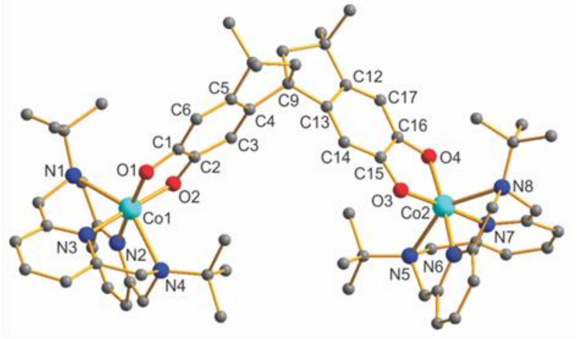

Figure 1. Structural representation of dinuclear Co complex **5** in **5a**. Color code: Co (cyan), O (red), N (blue), C (grey). Selected bond lengths (Å): Co1-O: 1.914(3) & 1.923(3); Co2-O: 1.888(3) & 1.904(3); Co1-N_{amine}: 2.329(3) & 2.355(3); Co2-N_{amine}: 2.310(3) & 2.356(3); Co1-N_{py}: 1.934(3) & 1.962(3); Co2-N_{py}: 1.919(3) & 1.945(3). Selected bond angles (˚): *trans* X-Co1-X = 148.3(1)-177.9(1); *trans* X-Co2-X = 148.4(1)-178.4(1); *cis* X-Co1-X = 76.7(1)-101.4(1); *cis* X-Co2-X = 76.6(1)-103.0(1). Data collected at 90 K.

Compound **5a** crystallizes in the triclinic space group *P*-1, with the entire dinuclear complex, tetrachlorocobaltate counteranion and solvent molecules in the asymmetric unit (Figure S1). Although good quality structural data were obtained at 90 K, poor diffraction inhibited efforts to obtain a room temperature structure. The dinuclear complex **5** is a V-shaped molecule reminiscent of the Me*n*tpa analogs **2** and **3**, with the spiro bis-dioxolene bridging the two cobalt centers such that a pseudo-twofold rotation axis passes through the spirocyclic carbon atom. Each cobalt center exhibits a highly distorted octahedral coordination geometry, with the remaining four coordination sites occupied by the N atoms of the L-N_4tBu_2 ligand. As was observed for the mononuclear complex **1**, the macrocyclic ligand binds such that the two sites *trans* to the O atoms of the bis-dioxolene are occupied by the pyridine N atoms. Detailed consideration of the metal and dioxolene-based structural parameters (Table S1) provides important insights into the spin and oxidation state of the cobalt centers as well as the oxidation state of the dioxolene moieties at the data collection temperature of 90 K. For the two cobalt centers, the Co-O, Co-N_{amine} and Co-N_{py} bond lengths are 1.907 ± 0.019, 2.338 ± 0.018 and 1.940 ± 0.022 Å, respectively, with the values for Co2 all a little shorter than those for Co1. Very useful reference complexes for comparing these Co-O/N distances are complex **1**, which was structurally characterized in both the low and high spin cobalt(II) forms, and a low spin cobalt(III)-catecholate analog with the related di-methyl substituted tetraazamacrocyclic ligand.[6] In general the Co/N bonds follow the trend: low spin cobalt(III) < low spin cobalt(II) < high spin cobalt(II), with six coordinate pseudo-octahedral low spin cobalt(II) also characterized by a Jahn-Teller distortion. In fact the Co-O/N distances measured for **5** in **5a** are all intermediate between the values expected for low spin cobalt(III) and low spin cobalt(II), with the Co-O and Co-N_{py} bonds in particular, much shorter than is generally observed for high spin cobalt(II). The dioxolene C-O and (O)C-C(O) distances in **5** are 1.317 ± 0.005 and 1.441 ± 0.001, which in comparison with bis-catecholate complex **2** and bis-semiquinonate complex **3**, are intermediate between the values generally observed for dioxolene ligands in the catecholate (C-O: 1.36(2) Å; (O)C-C(O) 1.41(2) Å) and semiquinonate state (C-O: 1.29(1) Å; (O)C-C(O) 1.46(2) Å).[10] An analysis including all of the dioxolene C-O and C-C bonds (Figure S2) following the method of Brown,[10] affords empirical metrical oxidation states (MOS) of -1.32 and -1.41 for the dioxolene moieties coordinated to Co1 and Co2, respectively, indicating a mixture of catecholate (MOS = -2) and semiquinonate (MOS = -1), with slightly more semiquinonate character. Assuming that complex **5** is a single species, the structural parameters determined at 90 K are most consistent with the formulation $[\{LS\text{-}Co^{III}(L\text{-}N_4tBu_2)\}spiro^{cat\text{-}sq}\{LS\text{-}Co^{II}(L\text{-}N_4tBu_2)\}]^{2+}$, with crystallographic disorder of the two halves of the complex giving rise to bond lengths intermediate between values expected for LS-Co^{III}-cat and LS-Co^{II}-sq moieties. Slight structural differences between the two halves of the molecule suggest more LS-Co^{III}-cat character for the Co2-containing half and more LS-Co^{II}-sq character for the Co1 half. The dicationic charge is consistent with the presence of a single tetrachlorocobaltate(2-) counteranion in the crystal structure and elemental analysis. The structural data may alternatively be interpreted as an equal mixture of $[\{LS\text{-}Co^{III}(L\text{-}N_4tBu_2)\}_2spiro^{cat\text{-}cat}]^{2+}$ and $[\{LS\text{-}Co^{II}(L\text{-}N_4tBu_2)\}_2spiro^{sq\text{-}sq}]^{2+}$ complexes, although magnetic and spectroscopic data (see later) exclude this possibility.

Variable temperature magnetic susceptibility data were collected for **5b** with applied magnetic fields of 87 Oe, 1 and 10 kOe over the temperature range 2-350 K (Figures 2 and S3), with data measured at the three fields essentially indistinguishable. At 2 K $\chi_M T$ is 1.9 $cm^3mol^{-1}K$, which sharply increases to a value of 4.8 $cm^3mol^{-1}K$ at 50 K and then remains steady until approximately 180 K, before again increasing to a value of 6.8 $cm^3mol^{-1}K$ at 350 K. Re-measuring upon cooling back down to 250 K reveals no significant hysteresis. The qualitative profile of the data is strongly reminiscent of that measured for the mononuclear cobalt(II)-semiquinonate complex **1**, which exhibits a low spin to high spin SCO transition at the cobalt(II) center above 200 K that is incomplete at 400 K.[6] The behavior is also very similar to that observed for a mononuclear oxazoline nitroxide complex of cobalt(II), which exhibits a SCO transition above 150 K.[11] In fact the data measured for **5b** can be interpreted as combination of contributions from the dinuclear complex **5** and the tetrachlorocobaltate(2-) counteranion, the contribution of which can be estimated from the temperature magnetic susceptibility profile measured previously for simple salts of tetrachlorocobaltate(2-).[12,13] In principle a tetrahedrally coordinated cobalt(II) center has a spin-only $S = 3/2$ ground state. For $g = 2$, the expected room temperature $\chi_M T$ value is 1.9 $cm^3mol^{-1}K$ (equivalent to a $\mu_{eff} = 3.9$) In fact salts of tetrachlorocobaltate typically exhibit magnetic moments in the range 4.6-4.8 (equivalent to $\chi_M T = 2.6\text{-}2.9$ $cm^3mol^{-1}K$) between

50 K and room temperature, due to distortion from tetrahedral symmetry giving rise to contributions from spin-orbital coupling and zero-field splitting.[12,13] The tetrachlorocobaltate(2-) anion of **5a** is similarly distorted from tetrahedral symmetry, with Co-Cl distances of 2.274(1)-2.310(1) Å and Cl-Co-Cl angles in the range 107.55(5)-112.77(4)° (Table S1), so the contribution of this complex is to the magnetic susceptibility data measured for **5b** is expected to be around $\chi_M T$ = 2.9 cm^{3}mol^{-1}K above 50 K. The remaining contribution to the magnetic susceptibility measured for **5b** arises from dinuclear complex **5** and can be related to the behavior of mononuclear analog **1**.[6] For complex **1** strong ferromagnetic coupling between the S = 1/2 semiquiononate radical and the S = 1/2 low spin cobalt(II) center affords an S = 1 ground state, with $\chi_M T$ measured as 1.2 cm^{3}mol^{-1}K in the temperature range 50-200 K, and the SCO transition observed above 200 K.[6] If complex **5** in **5b** is in the [{LS-Co^{III}(L-N$_4$$tBu_2$)spiro$^{cat\text{-}sq}${LS-Co^{II}(L-N$_4$$tBu_2$)}]$^{2+}$ form suggested by the 90 K X-ray diffraction data of **5a**, the $\chi_M T$ value of 4.8 measured between 50 and 200 K can be attributed to similar ferromagnetic coupling in the LS-Co^{II}-sq half of the dinuclear complex, in addition to a small fraction of trapped high spin cobalt(II), as was observed for **3** and **4**, as well as the contribution from the counteranion. Above 180 K the observed increase in $\chi_M T$ qualitatively resembles that of **1** and is most likely due to an incomplete SCO transition in the Co^{II}-sq half of the complex towards [{LS-Co^{III}(L-N$_4$$tBu_2$)spiro$^{cat\text{-}sq}${HS-Co^{II}(L-N$_4$$tBu_2$)}]$^{2+}$. It is also possible that the transition above 180 K is instead an incomplete VT transition at the LS-Co^{III}-cat half of the complex, which would afford [{HS-Co^{II}(L-N$_4$$tBu_2$)spiro$^{sq\text{-}sq}${LS-Co^{II}(L-N$_4$$tBu_2$)}]$^{2+}$. The magnetic data rule out the other possible interpretation of the 90 K X-ray data, i.e. that the sample is a mixture of [{LS-Co^{III}(L-N$_4$$tBu_2$)}$_2$spiro$^{cat\text{-}cat}$]$^{2+}$ and [{LS-Co^{II}(L-N$_4$$tBu_2$)}$_2$spiro$^{sq\text{-}sq}$]$^{2+}$, as these species would both be diamagnetic. Previously observed antiferromagnetic coupling between the spiro-bridged semiquinonate moieties in complexes with the diradical (spiro$^{sq\text{-}sq}$)$^{2-}$ ligand,[7] together with the effective two-fold symmetry of [{LS-Co^{II}(L-N$_4$$tBu_2$)}$_2$spiro$^{sq\text{-}sq}$]$^{2+}$, indicate that this species will be diamagnetic regardless of the nature of the coupling between the low spin cobalt(II) ion and the coordinated semiquinonate moiety.

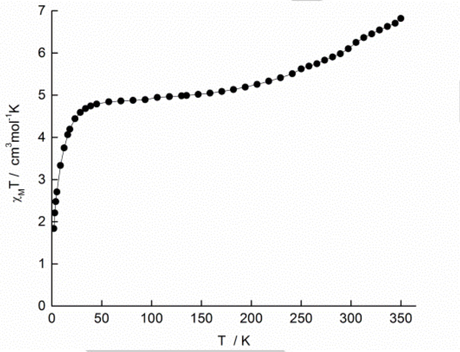

Figure 2. Variable temperature magnetic susceptibility data measured for **5b** with an applied magnetic field of 1 kOe. The line is to guide the eye.

Dissolution of **5b** in acetonitrile affords a blue solution, the UV-visible absorption spectrum (Figure S4) of which is dominated by bands between 580 and 700 nm that are due to the tetrachlorocobaltate(2-) ion.[13] Comparison with the spectra measured for HS-Co(II)-sq analog **3** is informative.[7] As is observed for **3**, the spectrum for **5b** exhibits a sharp band around 400 nm, which is assigned as an internal π to π^* transition of a semiquinonate ligand.[14] However, unlike **3**, the spectrum of **5b** does not show the strong bands between 500 and 750 nm that are characteristic of metal to ligand charge transfer for HS-Co(II)-sq complexes.[14] This indicates an absence of significant quantities of high spin cobalt(II) at room temperature in solution, which is consistent with the formulation [{LS-Co^{III}(L-N$_4$$tBu_2$)}spiro$^{cat\text{-}sq}${LS-Co^{II}(L-N$_4$$tBu_2$)}]$^{2+}$ proposed as the major species from 50 to 250 K.

Cyclic voltammograms (Figure 3) measured with a 1 mm glassy carbon electrode on a 1 mM solution of compound **5b** in acetonitrile (0.1 M Bu$_4$NPF$_6$) reveal multiple oxidative and reductive processes between -1.7 and 1.5 V versus ferrocenium/ferrocene. Within this potential window, two irreversible oxidative and two irreversible reductive processes (marked with an asterisk in Figure 3) are assigned to the tetrachlorocobaltate(2-) anion on the basis of literature studies in acetonitrile.[13,15] This leaves four irreversible oxidative (peak potentials: E_{pa} = 0.015, 0.17, 0.38 and 1.17 V) and two irreversible reductive waves (peak- potentials: E_{pc} = -0.85 and -0.99 V) that may be attributed to complex **5**. Again it is informative to compare the voltammetric data measured for **5b** with that reported for **2** and **3** (Figure S5).[7] The Me$_n$tpa analogs exhibit a pair of quasi-reversible one-electron oxidations (**2**) with $E_{1/2}$ = -0.15 and 0.008 V, or reductions (**3**) with $E_{1/2}$ = -0.70 and -0.86 V, which are associated with the (spiro$^{cat\text{-}cat}$)$^{4-}$ and (spiro$^{sq\text{-}sq}$)$^{2-}$ bridging ligands for **2** and **3**, respectively. This distinctive pair of processes is not evident for **5b** which may be due to a mixed-valent (spiro$^{cat\text{-}sq}$)$^{3-}$ redox state. With the present data it is impossible to definitively assign the processes as metal- or ligand-based, although it is clear that the redox chemistry is very rich and not inconsistent with the [{LS-Co^{III}(L-N$_4$$tBu_2$)}spiro$^{cat\text{-}sq}${LS-Co^{II}(L-N$_4$$tBu_2$)}]$^{2+}$ formulation proposed for **5**. Future UV-visible spectroelectrochemical studies will help to assign the redox processes and thus the redox state of the complex, although these would be best performed on an analog with a colorless and non-redox active counteranion to simplify assignment.

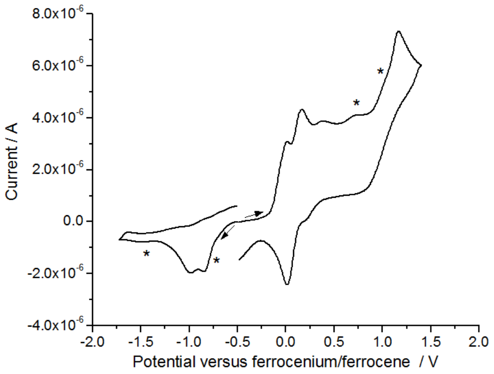

Figure 3. Cyclic voltammograms of **5b** in acetonitrile (1.0 mM with 0.1 M Bu$_4$NPF$_6$) measured with a 1.0 mm diameter glassy carbon working electrode

at a scan rate of 100 mVs^{-1}. Anodic and cathodic regions measured separately; asterisks mark processes attributed to the $[CoCl_4]^{2-}$.[13,15]

Conclusions

In summary, the preliminary study communicated herein clearly demonstrates that the dinuclear complex **5** exhibits very interesting electronic properties. These include mixed-valency, which is both metal- and ligand-based, as well as a thermally-induced SCO and/or VT transition. The structural, magnetic, spectroscopic and electrochemical data are all consistent with a formulation of $[\{\text{LS-Co}^{III}(\text{L-N}_4t\text{Bu}_2)\}\text{spiro}^{cat\text{-}sq}\{\text{LS-Co}^{II}(\text{L-N}_4t\text{Bu}_2)\}]^{2+}$ as the major species present for temperatures up to room temperature. There is no doubt that this complex is sufficiently interesting to warrant further study to fully elucidate the electronic structure and the nature of the thermally-induced transition as VT and/or SCO. However these studies would be greatly facilitated by the absence of a paramagnetic, redox-active and colored counteranion. Ongoing work in our laboratory is focused on the synthesis and investigation of salts of **5** with more innocuous counteranions, although obtaining pure crystalline samples is challenging. When they are in hand, detailed structural, spectroscopic, electrochemical and magnetochemical studies will be pursued. A high temperature crystal structure would also be invaluable for elucidation of the nature of the thermally-induced transition.

Experimental Section

Synthesis of 5: In an atmosphere of dry nitrogen gas, a solution of $CoCl_2{\cdot}6H_2O$ (0.354 g, 1.50 mmol) and L-N_4*t*Bu_2 (0.528 g, 1.50 mmol) in dry acetonitrile (10 ml) was refluxed for an hour. To this was added dropwise a warm solution of spiroH_4 (0.258 g, 0.750 mmol) and Et_3N (402 μL, 3.00 mmol) in acetonitrile. The nitrogen atmosphere was removed and air was bubbled through the solution until it was dark blue-green. After two days dark blue-green needle-shaped crystals grew on the glass wall of the vessel just above the level of the liquid and were rapidly isolated or mounted on the diffractometer to prevent redissolution. Crystals kept in contact with vapor from the mother liquor were identified as $[\{Co(L\text{-}N_4tBu_2)\}_2(spiro)][CoCl_4]{\cdot}5MeCN{\cdot}H_2O$ (**5a**) by single crystal X-ray diffraction, while air-drying causes partial desolvation and adsorption of atmospheric water to give $[\{Co(L\text{-}N_4tBu_2)\}_2(spiro)][CoCl_4]{\cdot}3H_2O$ (**5b**) in 0.10 g, 15 % yield. Although crystalline, **5b** was not suitable for single crystal X-ray diffraction. Elemental analysis calcd. (found) for **5b**, $Co_3C_{65}H_{90}N_8O_7Cl_4$: C, 55.20 (55.49); H, 6.41 (6.16); N, 7.92 (7.92); Cl, 10.03 (10.21) %. Selected IR data (KBr disk, cm^{-1}): 1604 (m), 1580 (w), 1513 (w), 1480 (w), 1433 (s), 1383 (w), 1363 (w), 1264 (w), 1226 (w), 1191 (s), 1169 (s), 1080 (s), 1030 (s), 937 (w), 912 (w), 850 (m), 791 (m). UV-vis (MeCN) λ / nm (ε / M^{-1}cm^{-1}): 400 (1850), 595 (540), 665 (680).

Crystal data for 5a: Formula $C_{75}H_{101}Cl_4Co_3N_{13}O_5$, $M_r = 1583.27$, triclinic, space group *P*-1, $a = 12.8857(5)$, $b = 16.2098(6)$, $c = 21.3060(7)$ Å, $\alpha = 100.945(3)$, $\beta = 100.108(3)$, $\gamma = 112.182(3)^\circ$, $V = 3893.5(3)$ Å^3, Z = 2, $\rho_{calcd} = 1.350$, $T = 89.9(6)$ K, = $\mu(CuK\alpha)$ 6.664 mm^{-1} ($\lambda = 1.54184$ Å), 24173 reflections measured, 12389 unique, refinement converged to $R = 0.0551$, $wR^2 = 0.1339$ ($I > 2\sigma(I)$), 926 parameters. CCDC-1418013 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge for the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article). Structural data (Table S1 and Figures S1 and S2), magnetic susceptibility data (Figure S3), electronic absorption spectra (Figure S4), electrochemical data (Figure S5).

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Keywords: spin crossover • valence tautomerism • mixed-valent compounds • redox-active ligands • magnetic properties

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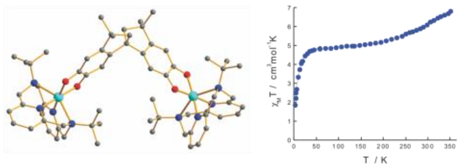

A dinuclear cobalt complex with a bridging bis-dioxolene ligand shows evidence for coinciding metal and ligand-based mixed-valence, as well as a thermally stimulated spin crossover or valence tautomeric transition.

Electronic lability

*A. Madadi, M. Itazaki, R. W. Gable, B. Moubaraki, K. S. Murray and C. Boskovic**

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